On the Reactions of Alkyl Halides with Sodium and Potassium Phenolates

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DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

H. C. ROBERTSON, JR.

BALTIMORE

1910

EASTON, PA.
ESCHENBACH PRINTING CO.
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ACKNOWLEDGMENT

The author takes pleasure in expressing his gratitude to President Remsen, Professor Morse, Professor Jones, Associate Professor Acree and Professor Andrews for instruction in the lecture room and laboratory. Especial thanks are due Associate Professor Acree, at whose suggestion this investigation was made.

On the Reactions of Alkyl Halides with Sodium and Potassium Phenolates.

In 1905 Brunel and Acree began an investigation[1] to learn whether in all ordinary, and catalyzed, chemical reactions involving electrolytes (acids, bases and salts) the ions as well as the nonionized forms are concerned. The fundamental investigations of Arrhenius[2] and Ostwald[3] and their students had placed the ionization theory on a sound footing, but had, perhaps unfortunately, also led chemists, with a few exceptions,[4] to believe that the *ions* are the only portions of electrolytes capable of entering into transformations.[5] The very

[1] Am. Chem. J., **27,** 118; **28,** 370; **31,** 185; **32,** 606; **37,** 71, 361; **38,** 1, 258, 489, 746; **39,** 124, 145, 226, 300; **41,** 457, 483; **42,** 115; **43,** 358, 505; **44,** 219; **48,** 352; **49,** 116, 345, 369. Ber. d. chem. Ges., **33,** 1520; **35,** 553; **36,** 3139; **37,** 184, 618; **41,** 3199. Science, **30,** 617 (1909). J. Am. Chem. Soc., **30,** 1755.

[2] Z. physik. Chem., **1,** 110, 631; **2,** 284; **4,** 226; **28,** 217, 326.

[3] J. prakt. Chem., [2] **27,** 1; **28,** 449; **29,** 406; **30,** 231; **31,** 307; **33,** 352; **35,** 112. Z. physik. Chem., **2,** 36, 136, 270.

[4] See especially Kahlenberg: J. Phys. Chem., **5,** 339; **6,** 1. Michael: Am. Chem. J., **43,** 322. Stieglitz: Cong. Arts and Sciences, St. Louis, 1904, and later papers. Acree: Am. Chem. J., **37,** 410; **38,** 258, and later papers.

[5] In recent years the application of these quantitative ideas to organic reactions has been used very successfully by a number of workers. In front rank stands the work of Stieglitz (Am. Chem. J., **39,** 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32,** 221; **34,** 1687. Congress Arts and Sciences, St. Louis, 1904) on the imido esters and their salts and his proof that the ions and nonionized substances are active. Especially important was his correlation of this work with the general problems of catalysis. Bredig (Z. Elektrochem., **9,** 118; **10,** 586; **11,** 528; **18,** 535, 539. Z. physik. Chem., **47,** 185) made a number of studies which he interpreted as reactions of ions, the best of which were perhaps his study of the catalysis of hydrogen peroxide by iodide ions, and of the decomposition of diazoacetic ester by hydrogen ions. The relation of this to the catalysis of esters through the activity of complex oxonium salts was discussed by him. Goldschmidt's work (Z. Elektrochem, **15,** 6. Z. physik. Chem., **60,** 728; **70,** 627; **81,** 30. Ber. d. chem. Ges., **39,** 711) on the esterification of organic acids

brilliancy of the new idea, together with the *apparent* evidence, and the authority of Arrhenius and Ostwald, dazzled chemists to such an extent that the possible activity of the nonionized substances was almost entirely neglected. When I began my work there was already some evidence that both the ions *and the nonionized forms* of acids, bases and salts are concerned in the well-known saponification of esters by acids and alkalies, in the inversion of cane sugar by acids, in the decomposition of diacetone alcohol by alkalies, in the formation of benzoin from benzaldehyde by potassium cyanide, in the inversion of menthone by sodium ethylate, in the rearrangement of acetylchloroaminobenzene by acids through the activity of the nonionized salt,

$$CH_3CONHClAnC_6H_5 \text{ (An = Cl, Br)}$$

and other cases discussed[1] in previous articles. All of these reactions had been assumed by others to involve only the hydrogen ions of the acid, the hydroxyl ions of the bases, or similar mechanisms.

The experimental evidence in all of these cases being in such condition that it could not be analyzed with absolute certainty, and the important factor of "salt catalysis" being so little understood, it was deemed wise to undertake the study of some typical organic reactions *in absolute ethyl alcohol* in order to measure all of the necessary factors with as high a degree of precision as possible. Ethyl alcohol was chosen as the solvent because in it the per cent. of ionization of different substances *varies far more* than in water, when the solutions are diluted from N/1 to N/2048. This fact is of the very greatest importance in studying the activity of the *nonionized electrolytes*, because *in N/1 alcoholic solutions, for instance, the concentration of the nonionized electrolyte is several times that found in the corresponding aqueous solutions, and the ac-*

in absolute ethyl alcohol proved the same general ideas and has formed, on account of its wealth of detail, one of our most important chapters. The work of Lapworth (J. Chem. Soc., **93,** 2163, 2203; **97,** 21; **99,** 1417, 2224; **101,** 2249; **103,** 252) on the influence of small amounts of water on esterification, conductivities, electromotive forces, and vapor pressures has formed one of our most brilliant chapters, because it furnished a much needed and far-reaching coördination of the physical properties and chemical activity of solutions, an example which should be followed by all chemists.

[1] For references see Am. Chem. J., **48,** 352; **49,** 348.

tivity of the nonionized electrolyte is therefore easily measured in most cases studied in this laboratory.

A few typical organic reactions were chosen for study, in some of which an electrolyte, for example an ethylate, was involved *purely catalytically* and was not decomposed during the chemical transformations, but in others of which the electrolyte was completely transformed into the end products. Such widely different cases were chosen to allow us to see whether the mechanism of the reaction is the same in both cases, both ions and nonionized electrolytes being involved alike in both classes of reactions. Our study of the *pure catalysis* of the reversible reaction

$$NaOC_2H_5 + RC : N + C_2H_5OH \rightleftharpoons NaOC_2H_5 + RC(:NH)OC_2H_5$$

by sodium, potassium and lithium ethylates, in which the ethylates are not changed into the end products, has shown that the mechanism of this reaction is essentially the same as that involving the sodium, potassium and lithium ethylates and methyl iodide or ethyl iodide, in which, of course, the ethylate is transformed into the end products:

$$C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + NaI$$

The evidence shows that the ethylates react in both cases through their ethylate ions as well as through their nonionized forms.

Another class of reactions studied by me and described in part in the present communication, and which have been found to be quite analogous to those involving ethylates and alkyl halides, are the changes involved when alkyl halides react with sodium, potassium and lithium phenolates in absolute ethyl alcohol:

$$C_6H_5ONa + ICH_3 \longrightarrow NaI + C_6H_5OCH_3$$

$$C_6H_5\overline{O} + ICH_3 \longrightarrow \overline{I} + C_6H_5OCH_3$$

The reactions proceed smoothly at 25° and 35° and the constants remain very regular throughout a large part of the transformation. The constants become from 3 to 5 per cent.

smaller toward the end of the change, probably because some of the alkyl halide may escape through the stoppers closing the flasks containing the reaction mixture, because the ether and sodium halides formed in the reaction suppress the ionization of sodium phenolate slightly, because there is probably a slight catalysis by the sodium halide formed, and especially because a small amount of the alkyl halide may form an olefin by a monomolecular reaction.[1] I have, therefore, disregarded at present the small decrease in the constants toward the end of the reaction and have considered the apparent course of the main reaction, which certainly seems to be bimolecular. I shall, however, study especially the side reaction involving the formation of olefins, along with the others.

In developing the equations[2] which we should use we may consider the case first in which the alkyl halide reacts with the phenolate anion. If these unite to form a complex anion in very *small traces*[3] and we represent the concentrations by the formulas, the equation

$$(a)\ CH_3I \times \overline{An} = K \times CH_3I.\overline{An}$$

holds *approximately* for any given concentrations even though the value of the "stability constant" K is not constant for all concentrations. We cannot experimentally[4] measure K at present and our only reason for thinking that K should remain constant for all concentrations is that the stability constants of most complex salts, such as double cyanides, complex ammonium salts, etc., are fairly constant. If this complex

[1] Brussoff (Z. physik Chem., **34,** 129) found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° form 16 per cent. of ethylene.

[2] The K_i and K_m used here may be the sum or product of other constants and may be made to include "salt effects" of ions or molecules; the "salt effect," however, seems fortunately to be small in this case.

Since it has been shown by Carrara (Gazz. chim. ital., **26,** I, 119; **33,** I, 241. Ahren's Sammlung, **12,** 403. Lapworth and Partington: J. Chem. Soc., **99,** 1417) that the ionic mobilities of sodium, potassium and lithium salts hardly change with concentration I shall assume, until my further work is completed, that $\alpha = \mu_v/\mu_\infty$ and that $\alpha(A - x)$ represents the ionic concentration of the sodium phenolate or sod um ethylate.

[3] For the development of these equations see Johnson and Acree: Am. Chem. J., **37,** 410; **38,** 258; **43,** 519; **48,** 352. Ber. d. chem. Ges., **41,** 3210, par. 1 and footnote 1, and p. 3214, par. 2, and other articles.

[4] I have planned some experiments to measure K.

yields the end products the following equations hold approximately, whether the complex salt is formed slowly (either reversibly or irreversibly) and decomposes rapidly, or is formed rapidly reversibly and decomposes slowly:

$$(b)\quad dx/dt = K'_i \times CH_3I.An = K'_i/K \times CH_3I \times An = K_i \times CH_3I \times An$$

But this is exactly the same equation that we get if the alkyl halide and anion react directly without the formation of an intermediate complex anion. In the one case our reaction velocity constant K'_i/K is the quotient of two constants, both of which (or the quotient) are assumed to be constant for all concentrations; in the other case we make no assumptions other than the constancy of the reaction velocity K_i.

In the present studies, however, the above equation fails to represent the entire reaction, and we may therefore consider the possibility of reactions of nonionized substances. It might well be that the *nonionized* double salt $C_2H_5I.NaOC_6H_5$ can decompose *in solution* into sodium iodide and phenyl ethyl ether just as Scholl[1] and Steinkopf have shown the *solid* (and presumably *nonionized*) cyanomethyl iodide-silver nitrate double compound to yield silver iodide and cyanomethyl nitrate. We may consider this nonionized double salt to be formed by the union of the alkyl halide with the anions and cations of the sodium phenolate, or by the union of the alkyl halide and nonionized sodium phenolate. These two processes are represented as follows:

$$(c)\quad C_2H_5I \times \overline{O}C_6H_5 \times \overset{+}{N}a = K' \times C_2H_5I.NaOC_6H_5$$

and

$$(d)\quad C_2H_5I \times NaOC_6H_5 = K'' \times C_2H_5I.NaOC_6H_5$$

It is clear that if sodium phenolate obeyed Ostwald's dilution law, and the equation

$$\overset{+}{N}a \times \overline{O}C_6H_5 = K''' \times C_6H_5ONa = \frac{K'}{K''} \times C_6H_5ONa$$

were true for all concentrations, K' and K'' also being constant,

[1] Ber. d. chem. Ges., **39**, 4393. Hantzsch and Caldwell: *Ibid.*, **39**, 2472. Acree and Loy: Am. Chem. J., **45**, 224.

we could not possibly tell which of these two processes is taking place. The reaction (*c*) would be written

$$(e)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= K_m/K'C_2H_5I \times OC_6H_5 \times Na$$
$$= \frac{K_mK''}{K'} \times C_2H_5I \times NaOC_6H_5 =$$
$$\frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

Equation (*e*) also represents the catalysis, by the sodium ions, of the reaction between the alkyl halide and the phenolate ions.

The reaction (*d*) would be written

$$(f)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= \frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

which would also hold even if no complex salt were formed as an intermediate product. If the sodium phenolate obeyed the Ostwald dilution law these two equations could be used interchangeably and we could not know whether the sodium phenolate reacts through the sodium and phenolate ions together, or through its nonionized portion, or through both processes together, and we could not know whether a ***negligible trace*** of the complex salt is an intermediate product.

Sodium phenolate apparently does not obey Ostwald's dilution law and these equations (*e*) and (*f*) are not identical by any means. If Equations (*b*) and (*c*) represent the true reactions the total reaction can be represented by the Equation (*g*) if α is the ionization and $(A - x)$ is the concentration of the sodium phenolate, and $(B - x)$ is the concentration of the alkyl halide at time t and $x = 0$ when $t = 0$.

$$dx/dt = K_i\alpha(A - x)(B - x) + K_m\frac{\alpha^2}{V}(A - x)(B - x)$$
$$= \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right](A - x)(B - x), \text{ or}$$

$$(g)\quad K_V = \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right]/V = \frac{B}{t(A - B)} \ln\frac{B(A - x)}{A(B - x)}$$

The Equation (*h*) holds if Equations (*b*) and (*f*) represent the two side reactions:

$$(h) \quad dx/dt = K_i\alpha(A-x)(B-x) + K_m(1-\alpha)(A-x)(B-x)$$
$$= [K_i\alpha + K_m(1-\alpha)](A-x)(B-x), \text{ or}$$
$$K_V = [K_i\alpha + K_m(1-\alpha)]/V = \frac{B}{t(A-B)} \ln \frac{B(A-x)}{A(B-x)}$$
$$= \frac{x}{t(A-x)}$$

when the concentrations of the sodium phenolate and alkyl halide are equal. Therefore

$$VK_V = K_N = K_i\alpha + K_m(1-\alpha)$$

for normal solutions of ionization α when $1/V$ is the concentration of the sodium phenolate.

It may be stated at once that Equation (*g*) has led to satisfactory constants in only two cases, those of the reactions between methyl iodide and sodium ethylate and potassium ethylate, whereas Equation (*h*) gives satisfactory constants in all of the cases studied up to this time. Whether in those two particular cases the methyl iodide does react with both ions together, perhaps along with the nonionized molecules, or whether it is an arithmetical accident cannot be said at present. Since some other hypotheses have not yielded satisfactory constants I shall confine myself at present to the discussion of Equation (*h*).

It is evident, then, that when the reaction velocities and ionic concentrations are measured in various solutions we have variations in K_N, α, $(1-\alpha)$, A and B. We can therefore determine the values of K_i and K *for normal solutions* from the series of simultaneous equations,

$$K_N = K_i\alpha + K_m(1-\alpha)$$
$$K'_N = K_i\alpha' + K_m(1-\alpha')$$
$$K''_N = K_i\alpha'' + K_m(1-\alpha''), \text{ etc.}$$

which are obtained by equating the values of K_N observed against the corresponding values of $K_i\alpha + K_m(1-\alpha)$, and substituting the proper values in Robertson's equations,

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}$$

and

$$K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha}$$

These two equations make it clear at once that K_m becomes zero when K_N is proportional to the ionic concentration of the salt. That is, if

$$K'_N : K_N = \alpha' : \alpha \quad \text{or} \quad K'_N\alpha - \alpha' K_N = 0$$

then

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha} = \frac{0}{\alpha' - \alpha}$$

Similarly, K_i becomes zero when K_N is proportional to the molecular concentration of the salt $(1-\alpha)$. That is, if

$$K'_N : K_N = (1-\alpha') : (1-\alpha)$$

then

$$K'_N(1-\alpha) - K_N(1-\alpha') = 0$$

and

$$K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha} = \frac{0}{\alpha' - \alpha}$$

Similarly, if $K_m = K_i$, then it follows that $K_N = K'_N$ and the velocity of the reaction, when referred to normal solutions, will not change with change in concentration.[1] In this case we find that $K_i = K_m = K_N$.

When we determine experimentally, with accuracy, the values of K_i and K_m by using two solutions of different concentrations we can calculate the reaction velocity at any other concentration. Smaller errors are involved when these two concentrations differ as widely as is experimentally advisable, the difference $\alpha' - \alpha$, etc., being then larger and smaller errors appearing in K_i and K_m. It is seen in Table XXVI that when N/1 and N/32 solutions are compared the values 0.0283 and 0.00476 are obtained for K_i and K_m, respectively, the average of all the values being 0.0282 and 0.00474. This agreement is excellent, but no better than was obtained in all the other work with other phenolates, and with sodium, potassium and lithium ethylates to be reported in another article.

[1] This case is approached closely in certain cases involved in the catalytic inversion of menthone by sodium ethylate, and the addition of alcohol to nitriles in the presence of sodium, potassium, lithium and tetramethylammonium ethylates, on which others will report soon.

All the possible combinations have been used in determining K_i and K_m and the results are given in Tables XXVI and XL for methyl iodide at 25° and 35°, and Tables LIII and LXIV for ethyl iodide at 25° and 35°. As can be seen, the variation in the values obtained for K_i and K_m is considerable, those for K_i in Table XXVI varying between 0.0264 and 0.0300 and those for K_m varying between 0.000372 and 0.00574 in the case of the reactions with methyl iodide at 25°, and those for K_i and K_m at 35° varying in a similar manner. This variation of about 50 per cent., in some cases, in the values of K_i and K_m may seem to indicate a very large experimental error in the determination of the reaction velocity, K_N, or the per cent. of ionization, α, of the phenolate salt, but such is not the case; the form of the equations, in which small differences, $\alpha' - \alpha$, etc., appear, is really responsible for such apparently large errors. The following example will illustrate the point: In Table XXV we find the values 0.01272 and 0.01447 for K_N for N/8 and N/16 solutions of sodium phenolate and methyl iodide at 25°. These values give 0.00574 as the value of K_m in Table XXVI. But if the values 0.01259 and 0.01462 had been used for K_N, the first being *decreased* therefore only 1.00 per cent. and the second being *increased* only 1.00 per cent., the value 0.00449 would have been found for K_m, which is *22 per cent. smaller* than the value 0.00574 actually obtained. It is perfectly apparent, then, that in this phenolate work, in which K_i is about six times as large as K_m, very small errors in K_N and α appear greatly magnified in the variations of K_i and K_m. In the work on the sodium ethylate, however, in which $K_i = 2.13\ K_m$ for methyl iodide, an error of one per cent. in K_N makes an error of only about 10 per cent. in K_m. For that reason there is much less variation in the individual values of K_i and K_m for sodium ethylate and methyl iodide, as can be seen in another article dealing with these substances.

It is best, therefore, to use (1) the average of *all* the values obtained for K_i and K_m, or (2) the average of the more accurate *starred* values obtained in those equations in which

$\alpha' - \alpha$ is larger, or (3) to combine all the simultaneous equations into one having the form

$$K_N + K'_N + K''_N + \ldots. =$$
$$K_i(\alpha + \alpha' + \alpha'' \ldots.) + K_m(1 - \alpha + 1 - \alpha' + 1 - \alpha'' + \ldots)$$

with which the individual equations are compared to get the values of K_i and K_m, and call these the closest approximation to the *true values*. It is seen in Table XXVI that the values obtained for K_i and K_m by these different methods all agree very closely. The values obtained for K_i and K_m in Tables XXVI, XL, LIII and LXIV were averaged and the average values substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$. In this way "calculated" values for K_N at every concentration were obtained and these are compared with the "found" values of K_N in Tables XXVII, XLI, LIV and LXV. It will be seen that the calculated and observed values are fairly concordant, agreeing almost within the limit of experimental error. This agreement is seen to be satisfactory when we recall that in these reactions in which the K_i is much greater than K_m small errors in the measurement of K_N cause great variations in the other two constants.

It is seen from Tables XXVI, XL, LIII and LXIV that sodium phenolate reacts with methyl iodide and ethyl iodide at 25° and 35° in a way that accords with the above equations. The values obtained for methyl iodide are $K_i = 0.0282$ and $K_m = 0.00474$ at 25° and $K_i = 0.091$ and $K_m = 0.0131$ at 35°, while the data for ethyl iodide are $K_i = 0.0056$ and $K_m = 0.00099$ at 25° and $K_i = 0.0184$ and $K_m = 0.00323$ at 35°.

If this theory is correct all phenolates should react with methyl and ethyl iodides in such a way that *the same value for K_i, after it is freed of all disturbing physical and "salt" effects, should be obtained for unit concentrations of a given alkyl halide and the phenolate ion, whatever its source, whereas different values could be found for K_m, the activity of the alkyl halide and the nonionized phenolate salt.* The nonionized sodium, potassium and lithium phenolates are *different substances* and can therefore *react with different velocities* with

methyl iodide or ethyl iodide. Now the best evidence for the validity of this theory is that the application of these equations to the data obtained by the use of all three of these phenolates gives us *nearly the same values* for K_i but *different values* for K_m.

Mr. J. H. Shrader has completed a series of investigations on potassium and lithium phenolates at 25° and 35° and finds values for K_i and K_m for methyl iodide and ethyl iodide which accord excellently with my data. A résumé of all the constants is given here:

Methyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0282	0.0047
Mr. Shrader	Potassium phenolate	0.0283	0.0037
Mr. Shrader	Lithium phenolate	0.0289	0.0039

Methyl Iodide and Sodium Phenolate at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.091	0.0131

Ethyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0056	0.00099
Mr. Shrader	Potassium phenolate	0.0052	0.00101
Mr. Shrader	Lithium phenolate	0.00534	0.00091

Ethyl Iodide and Different Phenolates at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0184	0.00323
Mr. Shrader	Potassium phenolate	0.0197	0.00270
Mr. Shrader	Lithium phenolate	0.0174	0.00319

When all of the data are analyzed carefully, and we consider the possibility of an "abnormal salt effect," and the fact that the results were obtained by two different workers, with different samples of materials, and different apparatus, and we remember especially the fact that relatively small experimental errors in K_N make large differences in K_i and K_m, as discussed on page 13, we see that the corresponding values for K_i agree well within the experimental errors. The values

for K_m vary considerably in many cases, in accordance with the theory. As I pointed out before, all of our work on the action of ethyl bromide, ethyl iodide and methyl iodide on sodium, potassium and lithium ethylates and on sodium phenyl-3-thiourazole harmonizes with the above experimental results and theory. We shall publish the details of all these investigations as quickly as possible.

The Study of Salt Catalysis

There is only one further point that needs discussion. It is seen from the foregoing pages that the reactions of sodium phenolate are not purely ionic, this transformation of the ions proceeding side by side with another involving, we believe, the nonionized salt. This deviation has been explained by Spohr[1] and Arrhenius,[2] and later by Lunden,[3] Euler,[4] Stieglitz,[5] and perhaps others, as an "auto effect" of the salt on the solvent or solution. I do not agree entirely with these workers and have explained my "salt catalysis" as due *chiefly* to the activity of the *nonionized salts* (the "normal" effect), augmented by a small "abnormal salt catalysis" resulting from changes in the physical properties of the solutions, and perhaps due partly to double compounds and to some role which electrons play. I am studying the question of "normal" and "abnormal" "salt catalysis" in connection with all these reactions, and I shall report my work later in detail when I study the reactions in concentrations varying from N/1 out to N/2048, especially in the presence of added salts. If there is an "abnormal salt effect" produced by the reacting phenolates, or metallic halides formed during the transformation, and such an effect can be analyzed by the equations

$$dx/dt = [1 + (f)C_{salt}][K_i\alpha + K_m(1 - \alpha)] \\ (C_{salt} - x)(C_{alkyl\ halide} - x)$$

in which $(f)C_{salt}$ is a function of the total salt (or its ions) as

[1] J. prakt. Chem., [2] **32**, 32; **33**, 265. Z. physik Chem., **2**, 194.
[2] *Ibid.*, **1**, 110; **4**, 226; **31**, 197.
[3] *Ibid.*, **49**, 195.
[4] *Ibid.*, **32**, 348. Ber. d. chem. Ges., **39**, 2726.
[5] *Loc. cit.*

expressed first by Spohr, Arrhenius and others, the correction of K_i and K_m for $(f)C_{salt}$ must be either negligible in *nearly all* of the above reactions or have the same general order of magnitude for all three salts and the same alkyl halide. Even if the latter is the case, no surprise should be occasioned if we remember the fact that the physical properties of the corresponding solutions of all the salts concerned are very much alike.

I should lay especial stress on the fact that in this laboratory we have obtained results from our study of "salt catalysis" in both *concentrated* and *dilute*, or *ideal*, *solutions* which make entirely insufficient all theories proposed hitherto to explain the peculiar effect which some neutral salts have on some reactions, but not on others. We prefer, therefore, to reserve for the future our final discussion of salt catalysis, and define later the actual form of the expression $(f)C_{salt}$ used above.

EXPERIMENTAL

Introduction

Conrad and Brückner[1] have already studied the reactions of sodium phenolate with alkyl halides, but their work with these compounds was not very extensive. The methods used by them in their study of reaction velocities have been somewhat modified in details which seemed to involve sources of error. These investigators, having made up solutions of phenolates and of alkyl halides of the desired strength, mixed their entire solutions at one time in a large flask and, at the expiration of the desired time-period, pipetted out portions and titrated these. This procedure necessitated opening the flask containing the reaction-mixture a number of times and produced a loss of the volatile alkyl halide, particularly at the relatively high temperatures. It has seemed preferable to vary this procedure and carry out each individual reaction in a separate small flask of a capacity only slightly larger than the volume of solution to be introduced. In this way possible loss of alkyl halide by volatilization is avoided.

Solutions of sodium phenolate were made up as follows: A

[1] Z. physik. Chem., **3**, 450; **4**, 273, 631; **5**, 289; **7**, 274, 283.

solution of sodium ethylate having twice the strength desired for the sodium phenolate was prepared by removing the crust from sodium under ligroin, removing the ligroin by dipping small pieces into alcohol a few seconds, and then dissolving this clean sodium in absolute alcohol at 0° in a graduated flask. After the solution was brought to the proper temperature, the proper titrations with standard acid and methyl orange, and the necessary dilution with absolute alcohol, gave the solution of desired strength. A solution of similar concentration of dry phenol in alcohol was also prepared. By mixing equal volumes of the two solutions, a solution of sodium phenolate of the desired strength was obtained. The contraction on mixing the two solutions is very small, but any decrease in volume may be made up for by diluting to the mark of the flask with alcohol, if a calibrated measuring flask is used to receive the mixed solutions.

Conrad and Brückner, in studying the reactions of phenolates, made up their solutions in a similar way. They assumed, however, that when sodium ethylate is mixed with its molecular equivalent of phenol, the reaction takes place as below:

$$C_2H_5ONa + C_6H_5OH \rightleftarrows C_6H_5ONa + C_2H_5OH$$

and that the reverse reaction is inappreciable.

It was found, however, in the present investigation, that such is probably not the case.[1] On mixing equivalents of sodium ethylate and phenol, solutions of sodium phenolate were obtained which did not give satisfactory constants when reacting with alkyl halides. There was a steady though slight decline in the reaction velocity even in short time-periods. Tables I and II illustrate this fact. The logical conclusion is that not all of the sodium ethylate has been converted into phenolate, and that we have the two substances reacting at the same time with the alkyl halide. Since the velocity con-

[1] The variation of the per cent. of alcoholysis with the change in concentration has not been studied carefully enough to allow me to make these slight corrections in the work reported here. This subject is being investigated as fully as possible. Mr. Shrader has already made a study of the velocity of reaction of methyl iodide with mixtures of sodium phenolate and sodium ethylate, the latter, of course, because of its higher ionization, suppressing the alcoholysis of the sodium phenolate more effectively than does the phenol.

stant of sodium ethylate is about three times that of the phenolate, it disappears more rapidly. This would account for the decrease observed. The phenol liberated suppresses largely the further alcoholysis of the phenolate, and the constants for the longer time-periods are about the same as those obtained when 1 or 2 per cent. excess of phenol was present in the original phenolate solution.

It was found that on the addition of an excess of phenol better constants were obtained. This is noticeable when only 1 per cent. excess is added (Tables XIII and XIV). On comparing these values, however, with those in which no excess of phenol is used, we see that the former are somewhat lower in numerical value. This led to the addition of more phenol and it was found that the decrease in the velocity constant was very great when large quantities of phenol were added. Tables I to X and XIII and XIV show the effects obtained by the addition of from 1 per cent. to 30 per cent. excess of phenol.

A study of the rise in boiling point caused by the addition of varying excesses of phenol to a normal solution of sodium phenolate in absolute alcohol has been made. This should throw light on the subject by showing whether or not there is a double salt formation when an excess of phenol is added to the solution of sodium phenolate. It was found that there was no appreciable amount of double salt present at the boiling temperature of the solution since the rise of boiling point was nearly proportional to the molecular excess added. It is possible that some double salt might be present at the temperatures at which the reactions were carried out and that this is almost completely broken down at the boiling temperature. The question will be investigated further. A study of the change in viscosity, caused by the addition of varying excesses of phenol, must be made before any explanation of the phenomenon can be attempted.

In Table XI I have given figures to show the relation between the velocity of reaction and the excess of phenol. The data are derived from Tables I to X and XIII and XIV, on the assumption that one per cent. of free phenol lowers the reaction velocity about 0.75 per cent. These values are all

for 0.5 N solutions of sodium phenolate and methyl iodide at 25°.

It seems that, in preparing solutions of sodium phenolate as described above, it is necessary to add at least a slight excess of phenol in order to convert all the sodium ethylate into phenolate. *In all my reactions I have therefore added an excess of one per cent. over the calculated quantity of phenol.* It is seen from Tables I and XV that the numerical values of the velocity constants are only slightly and consistently lowered by the addition of this small excess. We shall consider this subject again in our reports on the reactions in very dilute solutions.

Probable Causes for the Decrease in Velocity Constants as the Reactions near Completion

In practically all the reactions of the alkyl halides that have been studied it has been found that there is a steady, though slight, decrease in the velocity constants as the reaction progresses. It is seldom possible to obtain concordant values after fifty per cent. of the reacting substances have undergone change. It will be seen from my tables that I have relied mainly on the first half of the reactions for the best constants. The cause of this decrease in velocity constants has been attributed by many investigators to a loss of alkyl halide during the course of the reaction. The question has been taken up in the present investigation and it is certain that only a small part of this decrease can be attributed to the above source.

Solutions of methyl iodide (this being one of the most volatile alkyl halides used) were used for a study of the question. Standard solutions were prepared by weighing into a measuring flask nearly full of absolute alcohol a slight excess over the calculated amount of methyl iodide. The volume of alcohol necessary to bring the solution to the desired strength was then added from a pipette, both solution and alcohol, of course, being at the correct temperature.

A normal solution of methyl iodide was prepared as above and two 10 cc. portions were withdrawn *by suction with an ordinary pipette.* Each of these was added to an aqueous solu-

tion of silver nitrate in a tube which was at once sealed and heated at 60° for 24 hours. The results of these analyses showed that about one per cent. of the alkyl halide had been lost in the process of making up and transferring the solutions.

These results were confirmed by other analyses, in some cases the loss of methyl iodide being even larger. It should be stated that the alkyl halide had been previously analyzed and was undoubtedly quite pure.

From these experiments it was realized that unless precautions were taken to eliminate the error involved by loss of alkyl halide, the velocity constants in long time-periods might be seriously affected. A special form of pipette has been therefore devised which has proved itself invaluable in working with the alkyl halides and volatile liquids and gases in general. Fig. I shows in detail the construction and mechanism of this apparatus, which is mounted on a suitable brass frame (*F*), and held in position by plaster of Paris in the small, raised, hollow, brass boxes (*S*).

The 10 cc. or 20 cc. pipette (*A*) is surrounded by a jacket (*B*) through which water from the constant temperature bath is made to circulate by a Brown and Sharp rotary pump. The solution to be measured out is contained in the flask (*R*), which, together with the wash-bulbs (*W*), is immersed in the constant temperature bath. A two-valve blowing bulb is attached at (*G*). The wash-bulbs (*W*) are filled with a small quantity of the solution to be measured out, in order that the air going through them may be saturated with the alcohol and alkyl halide, and hence not take up any from the solution in (*R*) and cause a decrease in the concentration of the alkyl halide solution contained therein. The bulbs (*C*) catch any solution that may be accidentally forced from (*A*). If a compressed air system is at hand the bulbs (*C*) can be half filled with mercury, which is then forced up and down by the air under pressure. In this way the same air is always kept in (*A*) and the left bulb (*C*) and is always saturated.

To fill the pipette, stopcock (*N*) is turned so as to connect (*A*) with (*R*), and the three-way stopcock (*M*) is turned so as to furnish an outlet from (*A*) to the air. On pressing the

blowing bulb (*G*), the solution in (*R*) is forced into the pipette (*A*), the air which reaches the solution in (*R*) being saturated with the vapors of the alkyl halide and alcohol by passage through the wash-bulb (*W*). To deliver the pipette, stopcock (*M*) is turned so as to connect (*A*) with (*G*), (*W*) and (*R*). Stopcock (*N*) is turned so as to connect (*A*) with the capillary outflow tube (*H*). The liquid flows into the flask (*P*), the tip of the outflow tube (H) being held just under the surface of the sodium phenolate solution already in (*P*), and the pipette (*A*) is at the same time filled with the air which is already compressed in (*R*) and saturated with the vapor of the alkyl halide. The flasks (*P*) containing the sodium phenolate solutions are brought to the correct temperature in the bath before the alkyl halide solution is added, are kept at the right temperature in a beaker of water from the bath during the transfer of the alkyl halide, and are immediately closed with cork stoppers. The necks of the flasks are covered with "rubber fingers" to keep out water, and the flasks are then *shaken in the bath* to give the solutions perfect homogeneity and the correct temperature. When the capillary outflow tube (*H*) is well covered with binding tape or other insulating material there is no great difficulty in mixing the solutions at the desired temperature, 0°, 25° or 35°. This apparatus has been of great service in the work with alkyl iodides, solutions of ammonia, methylamine and other volatile substances. When it is used, the loss from volatilization is much less than is occasioned by the use of an ordinary pipette. I give the analyses which were made of three 10 cc. portions of methyl iodide measured out by the aid of the above device, many others having been made by Loy and Miss Brown. The alkyl halide solution was 0.3 per cent. stronger than normal.

Analyses	Percentage normal found	Percentage normal calculated
1	100.21	100.30
2	100.12	100.30
3	100.05	100.30

It is evident that the loss of methyl iodide involved when the apparatus described above is used is only 0.1 to 0.3 per

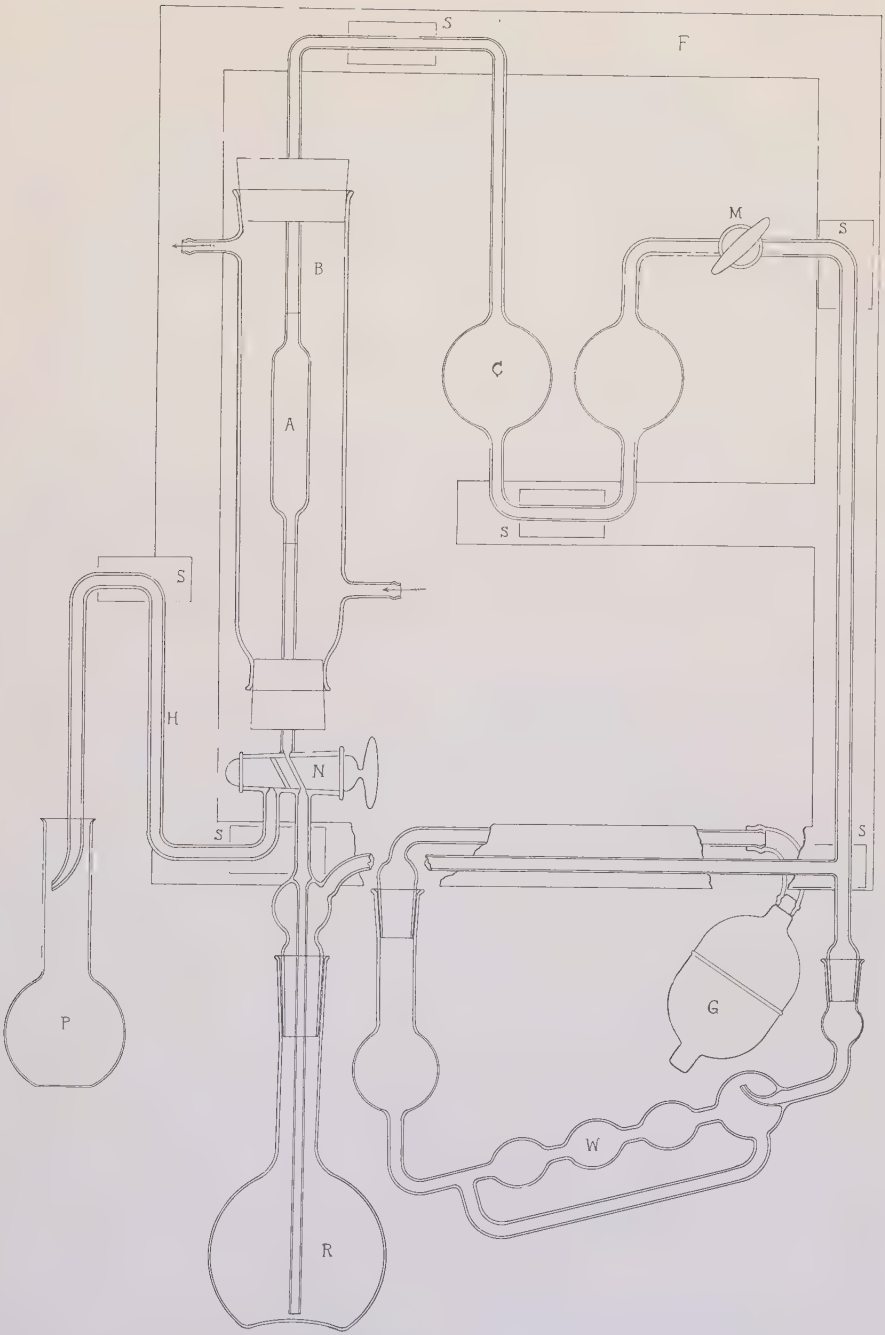

Fig. I

cent., which is much less than that incurred with the ordinary form of pipette, namely, about 1 per cent. Loy[1] has found that only about 0.1 per cent. of ethyl iodide is lost from N or 0.1 N solutions used in this apparatus. I have therefore always made the solutions of methyl iodide and ethyl bromide 0.3 per cent. too strong, and the solutions of ethyl iodide 0.1 per cent. too concentrated.

Experiments were carried out to determine whether alkyl halide is lost from the reaction flasks after they are stoppered and placed in the constant temperature baths. It was found that their weight did not decrease perceptibly even after standing a week. If alkyl halide escapes, we must assume that the same amount of water vapor enters through the stoppers, which is very improbable.

It is evident that the decrease in velocity constants noticed as the time-periods become longer cannot be attributed solely to loss of alkyl halide. At present it seems most probable that it is mainly due to a monomolecular side-reaction in which an olefin (or ether) is formed, because Brussoff[2] found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° give about 16 per cent. of the theoretical amount of ethylene. Since Brussoff did not exercise the very greatest care in freeing the olefins from the ethers formed simultaneously, we may consider this 16 per cent. a maximum amount at that temperature. There is certainly much less formed at lower temperatures; my own experiments show that there is a smaller decrease in the constants at 0° than at 25°. Furthermore, Johnson has carried out a large number of alkylations of the salts of urazoles at 60° in acetone, methyl alcohol and ethyl alcohol and has found evidence that the olefin formation is considerable, although not as much as 5 per cent. even when the reactions were 85 per cent. completed. In Johnson's work there was liberated one molecule of urazole acid for each molecule of olefin formed, according to the equation:

$$C_2H_5I + NaUr \longrightarrow C_2H_4 + NaI + UrH$$

and he was able to titrate this urazole acid with standard alkali,

[1] Loy: Dissertation, Johns Hopkins University, 1910.
[2] Z. physik. Chem., **34**, 129.

and hence calculate the amount of olefin formed. When this was done he was able to make a correction in his data and show that the velocity of the alkylation of the urazole salt was practically constant throughout. I cannot do this, however, in my work on the alkylation of phenolates and ethylates because the acids liberated, phenol and ethyl alcohol, are too weak to be titrated. We are therefore carrying out experiments to measure the amount of olefin formed, and shall then make the proper corrections in our data. We are, furthermore, studying the alkylations of the salts of urazoles and other fairly strong acids in absolute alcohol, and in this case we shall be able to study the amount of this side reaction by measuring the amount of urazole or other acid set free. We have evidence now that, notwithstanding the fact that added ether accelerates the reaction velocity, a small amount of the decrease in the velocity constant is due to the slight suppression of the ionization of the sodium phenolate by the sodium halide and ether formed in the reaction. The sodium phenolate and alkyl halides used, and the ethers and halide salts formed, change slightly the physical constants of the medium; the effects of solvation and viscosity on the ionic and molecular migration velocities, per cent. of ionization and reaction velocities will, therefore, be considered, but these effects seem to be counterbalanced in the present studies in such a way that the values for K_i and K_m are approximately the same for the concentrated as for the dilute solutions.

The amount of the decrease in the velocity constant is not over 3 to 5 per cent. even when the reaction is 75 per cent. complete, and in the first half of the reaction is hardly more than the unavoidable experimental errors. I have therefore disregarded this decrease in the present article and shall leave the further study of this point to the last refinement of my researches along these lines.

Preparation[1] *of Absolute Ethyl Alcohol*

With the exception of a few series of reactions carried out to determine the effect of traces of water on reaction velocity,

[1] We have been aided in this work on alcohol by a grant from the C. M. Warren Fund.

the solvent used was invariably nearly absolute alcohol. The work of numerous investigators[1] has shown that the effect of water on the velocity of reactions of this type may be a very important factor, and one that must be considered if accurate measurements are to be made. While the effect of traces of water on reactions between sodium phenolate and alkyl halides is not so great as in some other cases, it is nevertheless quite appreciable, and it seemed advisable to eliminate this factor by the use of solvents as free from moisture as it was practicable to obtain them. The dehydration of ethyl alcohol is a comparatively simple matter. The best commercial article was boiled several days with 400 grams of calcium oxide per liter of alcohol. After distillation, the treatment with calcium oxide was repeated, using a smaller proportion than before. The last traces of moisture were often removed by digesting the alcohol with turnings of metallic calcium and calcium oxide at 40°. At this temperature the metal is only slowly acted upon by alcohol, and the dehydration is very effective. After the first portion of calcium has passed into solution, second and third portions of about 10 grams or less per liter may be added and allowed to react at a moderate temperature. Such treatment will always be found sufficient to produce alcohol of a high degree of dehydration. I have used calcium oxide and calcium simultaneously because I found that metallic calcium alone increases the specific gravity when boiled some time with the alcohol. The increase in specific gravity is probably due to a catalytic decomposition of the alcohol into water and ethylene (or ether), which escapes. A sample of alcohol which had increased in specific gravity an amount corresponding to 0.18 per cent. water when treated with calcium was boiled with calcium oxide and was then found to contain only 0.03 per cent. of water. My best samples of alcohol have been obtained by the use of calcium oxide alone. I have found calcium carbide to be very effective in a short time. I shall report soon in another arti-

[1] Acree: Am. Chem. J., **41**, 457. Reid: *Ibid.*, **41**, 483. Goldschmidt and Sunde: Ber. d. chem. Ges., **39**, 711, and *loc. cit.* Joseph Gyr: *Ibid.*, **41**, 4322. Lapworth: J. Chem. Soc., **93**, 2163; *Loc. cit.* Bredig: *Loc. cit.* Biochem. *Z.*, **6**, 308. Ber. d. chem. Ges., **39**, 1756.

cle on some special apparatus and the methods found useful in preparing large quantities of pure alcohol.

Before the treatment with metallic calcium as above, the alcohol was invariably digested with 10 grams of silver nitrate or 3 grams of *m*-phenylenediamine hydrochloride per liter and distilled, after which it gave no decided tests for aldehydes.

It was found, in general, that the first treatment with calcium oxide gave alcohol of about 99.7 per cent. A second similar treatment in some cases gave alcohol of 99.99 per cent. purity. This was, however, only attained after several days' digestion at boiling temperature. It is much more convenient to remove the last traces of moisture with metallic calcium and calcium oxide.

It appears at present that specific gravity determinations made with a carefully calibrated pycnometer of at least 40 cc. capacity give the surest evidence of the dehydration of alcohol. The critical temperature of solution in kerosene, advocated by some investigators,[1] is hardly applicable as a test for absolute quantities of water, though it is certainly of great value in determining relative proportions. There is, necessarily, considerable variation, both in composition and dryness, between different samples of kerosene, and both factors are of essential importance. It was found that alcohol of specific gravity 0.78510 $\frac{25^\circ}{4^\circ}$, when mixed in equal volumes with a certain sample of commercial kerosene which had not been dried or distilled, gave a C. T. S. of 4°.02. With equal volumes of the same kerosene dried with calcium chloride and distilled the C. S. T. was —4°. Andrews suggests that kerosene used for this purpose be first treated by passing steam through it for a time to free it from its most volatile constituents and then dried and used. I have found that the C. T. S. of alcohol in kerosene so treated will vary greatly with the length of time that steam is passed through the kerosene. As an extreme instance, kerosene treated in this way for two days, when dried and distilled, gave with (approximately) 100 per cent. alcohol a C. T. S. = 12°, while the portion of

[1] See L. W. Andrews: J. Am. Chem. Soc., **30**, 353.

the oil which was volatile with water vapor, when dried, showed no cloudiness when mixed with an equal volume of 100 per cent. alcohol at a temperature of —8°. It is evident that the low boiling constituents of kerosene give with alcohol a much lower C. T. S. than the high boiling constituents and consequently variations in composition of kerosene will give corresponding variations of critical solution temperature. To use this method as a criterion of dehydration of alcohol would be hardly safe until one had set a standard for his particular sample of kerosene. I have relied entirely on the specific gravity method, and have made comparison tests by the kerosene method.

The pycnometer[1] used for the determination of specific gravity was of the Ostwald-Sprengel type and had a capacity of approximately 50 cc. It was provided with close-fitting, ground glass caps to prevent evaporation during weighing. This pycnometer was carefully calibrated several times and its capacity was known with a probable error of 0.0002 cc. It seems that little is to be gained by the use of a pycnometer larger than this unless one has a balance which is exceptionally sensitive under a heavy load. After bringing the pycnometer and its contents to the temperature of the bath, it was adjusted, wiped dry and allowed to stand some time in the balance case, when its weight was taken. In all my later work a duplicate pycnometer filled with water, whose caps were sealed on permanently with Khotinski wax, was carried through all these operations simultaneously and used as a *tare* in weighing. In this way errors due to deposition of moisture on the glass from the air were obviated. It is still better to avoid the use of caps on the tare by fusing the ends of the capillary tubes.

A number of samples of alcohol were dehydrated as above and their specific gravities were determined. The following values have been obtained within the last few months. In each case the alcohol was treated with silver nitrate and with calcium oxide twice besides the further treatment with calcium turnings and calcium oxide:

[1] The details of measurements with these and other types of pycnometers will be given in a monograph on alcohol.

Sample (1)	Treated with four portions of metallic calcium, sp. gr. =	0.785072
Sample (2)	Treated with calcium three times, sp. gr. =	0.785093
Sample (3)	Dried with calcium three times, sp. gr. =	0.785088
Sample (4)	Dried with calcium three times, sp. gr. =	0.785088
Sample (5)	Dried with calcium three times, sp. gr. =	0.785088
Sample (6)	Dried with calcium three times, sp. gr. =	0.785088
Sample (7)	Dried with calcium four times (middle portion of distillate), sp. gr. =	0.785069
Sample (8)	Dried with calcium six times (middle portion of distillate), *lowest sp. gr.* =	0.785058

It seems that under ordinary conditions anhydrous alcohol, obtained by the action of quicklime and calcium turnings on the commercial article, has a specific gravity of about 0.785085. By very complete dehydration and by fractional distillation somewhat lower figures may be obtained.

From this work it seems that the most probable value[1] for the specific gravity of alcohol is 0.78506 $\frac{25^\circ}{4^\circ}$. It should be stated that the specific gravity of water at 25° used for the above calculations was 0.997077, the value obtained by Chappuis,[2] and that the temperatures are on the hydrogen scale. Work on the physical constants of alcohol will be continued in this laboratory.

Purification of Alkyl Halides

Ethyl Iodide.—For the preparation of pure ethyl iodide, the best obtainable iodine was added to red phosphorus in 100 per cent. alcohol, and the resulting compound was washed well

[1] This value 0.78506 is identical with the one obtained by McKelvey and Osborne, of the National Bureau of Standards, in their very fine investigation on the physical properties of ethyl alcohol. See Circular No. **19** of the Bureau of Standards: Standard Density and Volumetric Tables.

[2] Thiesen: Wiss. Abh. Phys.-Techn. Reichsanst., **3**, 68 (1900). Chappuis: Bur. Int. d. Poids Mesures, Trav. Mém., **13** (1907).

with dilute alkalies and water. After drying it for a few minutes with calcium chloride, the dehydration was completed with a small quantity of resublimed phosphorus pentoxide. The alkyl halide was distilled from this through a dry condenser and again allowed to stand over phosphorus pentoxide. The dried liquid was subsequently redistilled several times in dried apparatus and thus obtained in good condition. The effect of light on the decomposition of these compounds being very marked, containing vessels of brown glass were used. By the addition of a few drops of mercury ethyl iodide may be kept entirely colorless. That there is no appreciable interaction between the two was shown by boiling ethyl iodide, under a return condenser, for three days with one-fifth its volume of mercury. Even with this vigorous treatment the action is slight, for it was found that only a little mercurous iodide was formed. On distilling the alkyl halide, a trace of mercury was found in the distillate. It is probable that at the boiling temperature a little mercury ethyl is formed, but, at ordinary temperatures, the quantity is not appreciable.

The boiling point of ethyl iodide[1] prepared as above was found to be 72°.14–72°.17 under 760 mm.

Methyl Iodide.—The methyl alcohol used in the preparation of methyl iodide contained about 0.1 per cent. water. Only the best iodine was used. Phosphorus pentoxide was used as above to remove the last traces of water and alcohol. After drying and redistilling, the methyl iodide was kept in dark bottles over a little mercury.

Since very discordant values are given by different authorities[2] for the boiling point and specific gravity of methyl iodide, careful determinations of both values were made. The thermometer used for the boiling-point determination was graduated in tenths of a degree. This thermometer was subsequently checked against a standard platinum resistance thermometer. The following values[3] were obtained:

[1] Mr. Meserve obtained 72°.20, and Mr. Shrader 72°.19, as the boiling point of ethyl iodide under 760 mm. at about 22°.

[2] Dobriner: Ann. Chem. (Liebig), **243**, 23. Perkin: J. prakt. Chem., [2] **31**, 500.

[3] Miss Brown obtained 42°.35, 42°.35, 42°.35–38, and 42°.31–36, as the boiling point of methyl iodide under 760 mm. at about 22°.

Sample I. Dried with phosphorus pentoxide and redistilled four times. B. p. = 42°.32—42°.34 under 759.35 mm. pressure

Sample II. Dried as above and redistilled twice. B. p. = 42°.25—42°.31 under 757.65 mm. pressure

The specific gravity of Sample (II) was found to be 2.2619 $\frac{25°}{4°}$.

Analysis:

0.7978 gram methyl iodide gave 1.3200 gram silver iodide.

	Gram found	Gram calculated
I	0.7135	0.7133

A number of analyses have shown that these alkyl halides can easily be prepared in a state of great purity, the foreign substances amounting to perhaps 0.01 to 0.05 per cent. The details will be given by Miss Brown and Messrs. Shrader and Meserve.

Phenol

The phenol used was Kahlbaum's best. It was twice redistilled and boiled from 180°.1 to 180°.2, uncorrected. After distillation it was pulverized and dried in vacuum desiccators over concentrated sulphuric acid for several weeks. After this treatment, it is improbable that more than traces of water were present. In making up solutions with phenol, care was taken not to expose it to the air more than was necessary, since it is quite hygroscopic and we desired to exclude all water from the reagents. A small box containing the balance, desiccator, flasks, etc., and fitted with a glass window, arm holes and rubber gloves, and also containing a drying agent, such as calcium chloride, through which the enclosed air is circulated by means of a fan, is quite necessary in transferring hygroscopic substances from the desiccator to the weighing tubes and volumetric apparatus. The temperature can also be regulated very easily. The apparatus will be described in detail in another article by Mr. Meserve.

Standard Acids and Alkalies

Hydrochloric acid was used for all titrations. It was standardized in several ways, all of which agreed satisfactorily.

The method of Acree and Brunel[1] is convenient and gives very satisfactory results. Dry, gaseous hydrochloric acid was passed into a flask containing a weighed quantity of water, precautions being taken to prevent loss of water vapor. The amount of acid absorbed was determined directly by weight and the solution thus obtained used as a standard in making up a large quantity of normal acid. In my most accurate work *weighed portions* were analyzed to within 0.01–0.02 per cent. and the correct volume determined by accurate measurements of the specific gravity.

Standard hydrochloric acid was also prepared by Hulett's method[2] and the results obtained were quite satisfactory. The acids obtained by these two methods were found to check one another within 0.1 per cent. Two gravimetric analyses of hydrochloric acid by Hulett's method were made, one giving 99.97 per cent. of the calculated weight of silver chloride and the other 100.07 per cent.

Standard sodium hydroxide was made from the purest metallic sodium by the use of sodium amalgam, and also by dropping small pieces of the sodium on ice water. It was thought that this gave a somewhat sharper titration with methyl orange than was given by alkalies containing carbonate. The alkali was standardized by titrating it against standard hydrochloric acid and also by evaporating a known volume with an excess of pure hydrochloric acid and weighing the residue of sodium chloride after ignition. Methyl orange was invariably used in all titrations.

Temperature Regulation

Constant temperatures were maintained by the use of two baths, the one for work at 25° having a capacity of about 450 liters, and the other for work at 35° having a capacity of 40 liters. Both were provided with efficient stirrers and there was no difficulty in keeping their temperatures permanently constant to within 0°.01, which was entirely satisfactory for reaction and conductivity work.

In making specific gravity determinations, however,

[1] Am. Chem. J., **36**, 117.

[2] Hulett and Bonner: J. Am. Chem. Soc., **31**, 390.

it was necessary to read temperatures somewhat closer than 0°.01. A Beckmann thermometer was therefore compared carefully with the standard and kept in the bath constantly for use in this work. In the pycnometric determinations of alcohol the temperature was read to within several thousandths of a degree and was probably correct to within 0°.004.

The standard thermometers used in this work have been calibrated to about 0°.002 at the National Bureau of Standards, or at the Bureau de Poids et Mesures at Sèvres, and have been checked by Dr. B. B. Turner in this laboratory against a standard platinum resistance thermometer of the Dickinson-Mueller type[1] as used in the United States Bureau of Standards, and somewhat modified by Dr. Turner and Acree. Our temperature standard is accurate to about 0°.002, which is much closer than we can rely upon any ordinary mercury thermometer. We shall describe later a special cathetometer and telescope, and the auxiliary apparatus, with which we can easily read primary standard thermometers to 0°.001 and good burettes to 0.001 cc.

Conductivity Measurements

The cells were of several types which we have designed in this laboratory and which will be described in another paper.[2] They seem to have an advantage over the older types in that they are far more constant and less subject to abrupt changes under careless handling.

The bridge wire, resistance box, etc., were carefully calibrated. Three readings of each resistance were taken at different points on the bridge wire and the results averaged, the mean values for the ionization μ_v/μ_∞ being given in Table XII. All conductivities are expressed in reciprocal ohms. The values used for μ_∞ were obtained by the direct measurement of the resistance of the N/2048, N/8096 and N/16182 solutions, which are practically completely ionized.

We have suspected for some time[3] that the differences in

[1] Bull. U. S. Bur. Standards., Vol. **3**, No. 4.

[2] Robertson and Acree: Address before the Int. Cong. Applied Chem., New York, September, 1912.

[3] Shadinger and Acree: Am. Chem. J., **39**, 231; **41**, 480, and later papers.

the viscosity of the different solutions will be found to have an influence on the velocity of movement of the different substances in solution and hence alter the reaction velocities in certain cases, and change the apparent per cent. of ionization of the various salts in the solution. If the ions of sodium ethylate move more slowly in the more viscous normal solutions than they do in the 0.1 N solutions, the conductivity measurements will not give us a true measure of the per cent. of ionization in the two cases. We should be compelled, therefore, to make a correction for the viscosity of the more concentrated solutions. No method is known at present, however, for doing this with certainty. One of us wrote of this problem to Professor A. A. Noyes, who at once kindly sent us two pages of a manuscript which he has since published.[1] Noyes' method is to multiply the apparent per cent. of ionization of the salt in a given solution by the ratio of the viscosity of this solution to that of the pure solvent. Dr. J. S. Guy has made measurements of the viscosities of various solutions of sodium ethylate, sodium phenolate, sodium iodide, and various mixtures of these, in absolute ethyl alcohol at 25° and 35°. The relation of the viscosities and conductivities of N, 0.5 N, and 0.25 N solutions of sodium phenolate and sodium ethylate, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the per cent. of ionization is the same for the N, 0.5 N and 0.25 N solutions. Such a conclusion is, however, not in harmony with all the known facts of physical chemistry and certainly not borne out by my experimental results. I have thought of using some formula such as the expression $\alpha \sqrt{\frac{V_N}{V_o}}$ in which V_o and V_N are the viscosities of the pure solvent and of the solution studied. Until further work can be done by the use of *other methods* to give us a direct measure of the real ionic velocities I do not see any clear way to solve this problem. I am at present trying to measure the conductivities, the viscosities by Bingham's methods and the migration velocities and solvation by Washburn's methods in order to learn the true per cent. of ionization of our com-

[1] Noyes and Lombard: J. Am. Chem. Soc., **33**, 1424. Washburn: *Ibid.*, **33**, 1464.

pounds. I have tried to apply Noyes' correction, as well as my own, in determining whether the formula $K_N = K_i\alpha + K_m \frac{(\alpha)^2}{V}$ gives us constants for K_i and K_m when such correction is made (see page 9). The results have not been at all satisfactory. The best plan is to work with solutions which are so dilute that the viscosities are all practically the same as that of the pure solvent. It can be seen how great the difficulty is in making such a correction when it is realized that the viscosity of a N solution of sodium phenolate or sodium ethylate is nearly three times as large as that of the pure ethyl alcohol, and that the viscosity of our reaction mixtures is constantly changing. We have therefore extended our studies in this laboratory to regions as dilute as can possibly be measured with reasonable accuracy. It is a peculiar fact that our constants for K_i and K_m are practically the same for N solutions as for the dilute solutions, and we may find on further work that the "viscosity effects" influence the reaction velocities and the conductivities in such a way as to annul the errors discussed above. This field is a bright one for investigation. It is very fortunate for others who work with aqueous solutions that the viscosity of their most concentrated solutions is not greatly different from that of water; the errors cannot be very great in any case. We are measuring the viscosities of all of our solutions before and after the reactions are complete, and even during the reactions, to collect data which may shed light on this problem. I have also measured the change in volume in a number of cases, and have attempted to use the dilatometer in some cases to follow the velocity of the reaction. If the solution changes in volume there will be a corresponding change in the concentrations, for which we must make corrections. Certain energy changes will also be involved in the change of volume and these may be of great interest in the future. As I have pointed out before, chemists should consider in these studies every possible chemical and physical factor.

Measurements and Calculations of Reaction Velocities

The reactions were interrupted at the end of the desired

time-period by removing the small flask from the bath and pouring its contents into 200 cc. of cold distilled water, after which the titration with standard 0.2 N or 0.1 N hydrochloric acid was immediately made, and the amount of unchanged sodium phenolate thus determined. It was found by experiment that the above procedure involved no appreciable error, the progress of the reaction being practically reduced to zero by dilution with the large volume of cold water.

In the tables which follow, the constants have been calculated from the equations:

(1) $K_N/V = K_V = \frac{1}{t} \cdot \frac{x}{A - x}$ (for equivalent masses)

and

(2) $K_N/V = K_V = \frac{B}{t(B - A)} \log_n \frac{B(A - x)}{A(B - x)}$ (for unequal masses)[1]

In this way both sets of velocity constants are referred to the same basis and become comparable.

The values given for A generally represent the actual volumes in cc. of the sodium phenolate solutions used. Under x is given the number of cc. of standard acid required for each titration, *referred to the same normality as the sodium phenolate solution used in that particular series of reactions.* These values of x therefore actually represent the volumes of A that have disappeared at the end of each time-period. K_N represents the velocity constant for each series when referred to the normal basis. It is obtained by multiplying the constant K_V by the dilution, V, in liters, of the sodium phenolate after mixture with the alkyl halide solution.

Summary

Tables I to XI and XIII and XIV illustrate the decrease in velocity of the reaction as increasing excesses of phenol are added. The general relations are shown in Table XI.

In Table XII we give the approximate ionization of sodium phenolate at 25° and 35° in solutions varying from N/1 to N/32. These have not yet been corrected for the influence of viscosity and solvation.

[1] Hecht, Conrad and Brückner: Z. physik. Chem., **3**, 455.

Tables XIII to XXIV show the velocities of the reactions of sodium phenolate and methyl iodide at 25° in solutions varying from N/1 to N/32. Table XXV gives the average values for K_N, Table XXVI gives the values for K_i and K_m, and Table XXVII gives the values for "K_N found," "K_N calculated," and the experimental errors.

Tables XXVIII to XXXVIII give the velocity of transformation of sodium phenolate and methyl iodide at 35° in solutions varying from N/2 to N/40. Table XXXIX gives the average values for K_N, Table XL gives the values for K_i and K_m and Table XLI gives the values of "K_N found," "K_N calculated" and the experimental errors.

Tables XLII to LI give the reaction velocities for sodium phenolate and ethyl iodide at 25° in solutions varying from N/1 to N/16. Table LII gives the average values for K_N, Table LIII gives the values for K_i and K_m, and Table LIV gives the values "K_N found," "K_N calculated," and the experimental errors.

Tables LV to LXII give the reaction velocities for sodium phenolate and ethyl iodide at 35° in concentrations varying from N/2 to N/16. Table LXIII gives the average values of K_N, Table LXIV gives the values of K_i and K_m and Table LXV gives the values for "K_N found," "K_N calculated," and the experimental errors.

Table LXVI gives a résumé of all the values for K_i and K_m.

THE EFFECT OF AN EXCESS OF PHENOL ON THE REACTION VELOCITY AT 25°

Table I—0.5 N Sodium Phenolate and 0.25 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.02$

t	x	K_V
30	1.28	0.00488
40	1.62	0.00482
50	1.90	0.00468
60	2.16	0.00458
80	2.66	0.00452
100	3.09	0.00446

Average $K_V = 0.00466$

Table II—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
40	1.62	0.00483
50	1.95	0.00484
60	2.17	0.00462
80	2.70	0.00462
100	3.14	0.00458
140	3.86	0.00449

Average $K_V = 0.00466$

For Reactions with 1 per cent. Excess Phenol, see Tables XII and XIII.

Table III—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
30	1.22	0.00463
40	1.54	0.00455
50	1.88	0.00463
65	2.31	0.00462
75	2.54	0.00454
90	2.84	0.00441

Average $K_V = 0.00456$

Table IV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
30	1.20	0.00454
40	1.53	0.00451
50	1.86	0.00457
60	2.14	0.00454
70	2.44	0.00460
100	3.09	0.00447

Average $K_V = 0.00454$

Table V—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

$A = 10.04$

t	x	K_V
30	1.15	0.00431
40	1.47	0.00428
50	1.77	0.00428
60	2.06	0.00430
70	2.32	0.00429
90	2.99	0.00428

Average $K_V = 0.00429$

Table VI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

$A = 10.01$

t	x	K_V
30	1.16	0.00436
40	1.48	0.00434
50	1.79	0.00435
60	2.06	0.00432
100	3.04	0.00436

Average $K_V = 0.00435$

Table VII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

$A = 10.04$

t	x	K_V
20	0.76	0.00409
30	1.12	0.00418
40	1.42	0.00412
50	1.73	0.00416
60	1.98	0.00409
80	2.48	0.00410

Average $K_V = 0.00412$

Table VIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

$A = 10.05$

t	x	K_V
20	0.754	0.00406
30	1.106	0.00412
40	1.44	0.00418
50	1.69	0.00404
60	1.97	0.00406

Average $K_V = 0.00409$

Table IX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (20 per cent. Excess Phenol) at 25°

$A = 10.01$

t	x	K_V
20	0.71	0.00382
40	1.34	0.00386
50	1.65	0.00395
60	1.90	0.00390
90	2.62	0.00395
260	5.05	0.00391

Average $K_V = 0.00390$

Table X—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (30 per cent. Excess Phenol) at 24°.95

$A = 10.01$

t	x	K_V
30	0.99	0.00365
40	1.28	0.00367
50	1.57	0.00372
60	1.80	0.00365
80	2.27	0.00366
100	2.69	0.00367
123	3.10	0.00365

Average $K_V = 0.00367$

Table XI—Resume of the Reaction Velocities for 0.5 N Sodium Phenolate, 0.5 N Methyl Iodide and an Excess of Phenol at 25°

Excess of phenol in per cent.	K_V	K_V calculated
0	0.00466	0.00467
1	0.00462	0.00463
2	0.00455	0.00460
5	0.00432	0.00450
10	0.00410	0.00432
20	0.00390	0.00397
30	0.00367	0.00362

Table XII—The Ionization of Sodium Phenolate at 25° and 35°

Ionization at 25°

V	α	$1-\alpha$
1	0.122	0.878
2	0.189	0.811
4	0.258	0.742
8	0.335	0.665
16	0.419	0.581
32	0.509	0.491

Ionization at 35°

V	α	$1-\alpha$
2	0.185	0.815
4	0.247	0.753
8	0.319	0.681
16	0.399	0.601
32	0.486	0.514
40	0.516	0.484

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 25°

Table XIII—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
20	1.33	0.00780
30	1.87	0.00766
40	2.35	0.00767
50	2.78	0.00770
60	3.14	0.00762
80	3.75	0.00750

Average $K_V = 0.00766$
$K_N = 0.00766$

Table XIV—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
20	1.34	0.00773
30	1.87	0.00766
40	2.34	0.00764
50	2.74	0.00755
60	3.11	0.00752

Average $K_V = 0.00762$
$K_N = 0.00762$

Table XV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	1.24	0.00471
40	1.56	0.00462
51	1.91	0.00462
60	2.18	0.00464
70	2.45	0.00464
80	2.66	0.00452
100	3.14	0.00457

Average $K_V = 0.00462$
$K_N = 0.00924$

Table XVI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

$A = 9.98$

t	x	K_V
21	0.91	0.00478
30	1.22	0.00464
40	1.56	0.00463
50	1.88	0.00465
60	2.16	0.00460
80	2.65	0.00452
120	3.52	0.00454

Average $K_V = 0.00462$
$K_N = 0.00924$

Table XVII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	0.736	0.00265
40	0.98	0.00271
50	1.18	0.00267
60	1.39	0.00269
70	1.56	0.00264
82	1.77	0.00262
150	2.80	0.00259

Average $K_V = 0.00265$
$K_N = 0.01060$

Table XVIII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$

t	x	K_V
50	1.20	0.00273
60	1.41	0.00274
70	1.59	0.00270
90	1.92	0.00265
100	2.12	0.00269
110	2.29	0.00269

Average $K_V = 0.00270$
$K_N = 0.01080$

Table XIX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 10.00 B = 20.00

t	x	K_V
40	1.18	0.00162
54	1.52	0.00159
65	1.78	0.00158
75	1.99	0.00156
85	2.22	0.00157
100	2.52	0.00156

Average K_V = 0.00158
K_N = 0.01264

Table XX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 10.00 B = 20.00

t	x	K_V
40	1.20	0.00165
50	1.44	0.00161
60	1.66	0.00158
70	1.91	0.00159
80	2.14	0.00160
100	2.56	0.00158

Average K_V = 0.00160
K_N = 0.01280

Table XXI—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 10.00 B = 40.00

t	x	K_V
40	1.32	0.000900
50	1.66	0.000928
60	1.90	0.000900
70	2.20	0.000914
80	2.42	0.000894

Average K_V = 0.000907
K_N = 0.01451

Table XXII—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 20.00 B = 80.00

t	x	K_V
50	3.27	0.000912
60	3.84	0.000911
70	4.34	0.000909
80	4.87	0.000901
90	5.33	0.000893
100	5.79	0.000889

Average K_V = 0.000902
K_N = 0.01443

Table XXIII—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 20.00 B = 160.00

t	x	K_V
70	5.06	0.000529
80	5.63	0.000525
90	6.24	0.000529
100	6.69	0.000520
110	7.20	0.000520
120	7.67	0.000517

Average K_V = 0.000523
K_N = 0.01674

Table XXIV—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 20.00 B = 160.00

t	x	K_V
60	4.51	0.000539
70	5.03	0.000525
80	5.60	0.000523
90	6.16	0.000522
100	6.69	0.000520

Average K_V = 0.000526
K_N = 0.01683

Table XXV—K_N Found for Sodium Phenolate and Methyl Iodide at 25°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
1	0.00766	
	0.00762	0.00764
2	0.00924	
	0.00924	0.00924
4	0.01060	
	0.01080	0.01070
8	0.01264	
	0.01280	0.01272
16	0.01451	
	0.01443	0.01447
32	0.01674	
	0.01683	0.01678

Table XXVI—K_i and K_m Found for Sodium Phenolate and Methyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0286	0.00473
$V = 1 : V = 4$	0.0274†	0.00489†
$V = 1 : V = 8$	0.0286*	0.00473*
$V = 1 : V = 16$	0.0278*	0.00483*
$V = 1 : V = 32$	0.0283*	0.00476*
$V = 2 : V = 4$	0.0264	0.00524
$V = 2 : V = 8$	0.0286†	0.00473†
$V = 2 : V = 16$	0.0276*	0.00494*
$V = 2 : V = 32$	0.0283*	0.00478*
$V = 4 : V = 8$	0.0300	0.00393
$V = 4 : V = 16$	0.0281†	0.00466†
$V = 4 : V = 32$	0.0286*	0.00445*
$V = 8 : V = 16$	0.0266	0.00574
$V = 8 : V = 32$	0.0282†	0.00490†
$V = 16 : V = 32$	0.0294	0.00372
Average	0.0282	0.00474
Average[1]	0.02815	0.00477
Average[2]	0.0282	0.00475

[1] The average of all the values with daggers and asterisks.
[2] The average of all the values with asterisks.

Table XXVII—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 25°

V	α	$1-\alpha$	K_N found	K_N calculated	Error in per cent.
1	0.122	0.878	0.00764	0.00760	+0.5
2	0.189	0.811	0.00924	0.00917	+0.8
4	0.258	0.742	0.01070	0.01079	—0.8
8	0.335	0.665	0.01272	0.01260	+1.0
16	0.419	0.581	0.01447	0.01457	—0.7
32	0.509	0.491	0.01678	0.01668	+0.6

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 35°

Table XXVIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
20	2.18	0.01397
30	2.93	0.01385
40	3.55	0.01381
50	4.08	0.01383
60	4.50	0.01368

Average $K_V = 0.01383$

$K_N = 0.02766$

Table XXIX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	2.98	0.01412
40	3.60	0.01406
50	4.13	0.01407
60	4.53	0.01381
72	4.96	0.01367
85	5.42	0.01392

Average $K_V = 0.01394$

$K_N = 0.02788$

Table XXX—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	2.44	0.00808
50	2.86	0.00808
60	3.21	0.00791
70	3.59	0.00802
100	3.89	0.00798
	4.39	0.00785

Average $K_V = 0.00798$

$K_N = 0.03192$

Table XXXI—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	1.94	0.00802
40	2.43	0.00802
50	2.84	0.00793
60	3.23	0.00795
70	3.58	0.00795
80	3.89	0.00793

Average $K_V = 0.00797$

$K_N = 0.03188$

Table XXXII—0.125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
50	1.98	0.00493
60	2.24	0.00481
70	2.52	0.00481
80	2.77	0.00482
90	2.98	0.00472

Average $K_V = 0.00482$
$K_N = 0.03856$

Table XXXIII—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 20.00$

t	x	K_V
20	1.66	0.00474
30	2.42	0.00492
40	3.02	0.00490
50	3.52	0.00481
60	3.95	0.00472
70	4.39	0.00472

Average $K_V = 0.00480$
$K_N = 0.03840$

Table XXXIV—0.0625 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 40.00$

t	x	K_V
75	6.34	0.00278
80	6.72	0.00282
90	7.30	0.00281
100	7.84	0.00279
110	8.24	0.00281

Average $K_V = 0.00280$
$K_N = 0.04480$

Table XXXV—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 39.904$

t	x	K_V
45	3.815	0.00281
55	4.373	0.00279
65	4.821	0.00272
75	5.331	0.00276
85	5.674	0.00269
95	6.010	0.00266

Average $K_V = 0.00274$
$K_N = 0.0444$

Table XXXVI — 0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	10.37	0.00158
70	11.36	0.00156
80	12.35	0.00157
90	13.32	0.00160

Average $K_V = 0.00158$
$K_N = 0.05056$

Table XXXVII—0.03125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	6.37	0.00167
70	7.04	0.00163
80	7.78	0.00162
100	8.96	0.00159
110	9.60	0.00159

Average $K_V = 0.00162$
$K_N = 0.0518$

Table XXXVIII — 0.025 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 40.00 \quad B = 400.00$

t	x	K_V
45	17.96	0.00136
75	24.60	0.00132
90	27.50	0.00134
110	29.80	0.00130

Average $K_V = 0.00133$
$K_N = 0.0532$

Table XXXIX—K_N Found for Sodium Phenolate and Methyl Iodide at 35°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
2	0.02766 0.02788	0.02777
4	0.03192 0.03188	0.03190
8	0.03856 0.03840	0.03843
16	0.04480 0.04440	0.04460
32	0.05056 0.05180	0.05120
40	0.05320	0.05320

Table XL—K and K_m Found for Sodium Phenolate and Methyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.082	0.0155
$V = 2 : V = 8$	0.093	0.0130
$V = 2 : V = 16$	0.092	0.0133
$V = 2 : V = 32$	0.093	0.0134
$V = 4 : V = 8$	0.101	0.0093
$V = 4 : V = 16$	0.095	0.0113
$V = 4 : V = 32$	0.092	0.0120
$V = 8 : V = 16$	0.090	0.0141
$V = 8 : V = 32$	0.090	0.0143
$V = 16 : V = 32$	0.090	0.0143
$V = 2 : V = 40$	0.090	0.0136
$V = 4 : V = 40$	0.091	0.0123
$V = 8 : V = 40$	0.089	0.0144
Average	0.091	0.0131

Table XLI—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.0278	0.0275	+1.1
4	0.0319	0.0323	—1.2
8	0.0385	0.0379	+1.6
16	0.0448	0.0442	+0.9
32	0.0506	0.0509	+0.6
40	0.0532	0.0533	—0.2

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 25°

Table XLII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.96$

t	x	K_V
50	0.712	0.00154
60	0.86	0.00157
80	1.09	0.00153
95	1.285	0.00158
120	1.54	0.00153

Average $K_V = 0.00155$

$K_N = 0.00155$

Table XLIII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	0.455	0.001554
43	0.626	0.001552
57	0.830	0.001584
68	0.954	0.001551
79	1.090	0.001548
90	1.226	0.001553

Average $K_V = 0.001557$

$K_N = 0.001557$

Table XLIV—0.5 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
30	0.54	0.000937
50	0.86	0.000919
60	1.01	0.000912
70	1.19	0.000932
80	1.34	0.000932

Average $K_V = 0.000926$

$K_N = 0.001852$

Table XLV—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
60	0.530	0.000930
70	0.610	0.000928
80	0.710	0.000955
90	0.770	0.000927
100	0.836	0.000912
110	0.908	0.000908

Average $K_V = 0.000927$

$K_N = 0.001854$

Table XLVI—0.25 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.98$ $B = 39.92$

t	x	K_V
30	0.65	0.000566
45	0.96	0.000568
60	1.186	0.000534
70	1.33	0.000518
90	1.70	0.000529
115	2.18	0.000550

Average $K_V = 0.000544$
$K_N = 0.002176$

Table XLVII—0.25 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
70	0.71	0.000527
80	0.80	0.000532
90	0.91	0.000543
100	0.99	0.000535
110	1.11	0.000550
120	1.20	0.000550

Average $K_V = 0.000546$
$K_N = 0.002184$

Table XLVIII—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 40.00$

t	x	K_V
60	0.71	(0.000309)
70	0.85	0.000320
80	0.95	0.000316
90	1.06	0.000316
100	1.18	0.000318
110	1.27	0.000313

$K_V = 0.0003166$
$K_N = 0.002533$

Table XLIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	1.44	0.000322
70	1.68	0.000317
80	1.91	0.000317
90	2.14	0.000319
100	2.35	0.000317
110	2.54	0.000315

Average $K_V = 0.000318$
$K_N = 0.002544$

Table L—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 80.00$

t	x	K_V
61	0.84	0.000181
75	1.04	0.000184
90	1.25	0.000187
105	1.42	0.000184
120	1.58	0.000180
140	1.80	0.000179

Average $K_V = 0.000182$
$K_N = 0.00292$

Table LI—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	1.68	0.000184
70	1.91	0.000181
80	2.15	0.000180
90	2.40	0.000179
100	2.64	0.000178

Average $K_V = 0.0001804$
$K_N = 0.00289$

Table LII—K_N Found for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N	Average K_N
1	0.00155 0.00156	0.00155
2	0.00185 0.00185	0.00185
4	0.00216 0.00218	0.00217
8	0.00254 0.00254	0.00254
16	0.00289 0.00292	0.00290

Table LIII—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0055	0.00100
$V = 1 : V = 4$	0.0056	0.00099
$V = 1 : V = 8$	0.0056	0.00098
$V = 1 : V = 16$	0.0058	0.00099
$V = 2 : V = 4$	0.0056	0.00097
$V = 2 : V = 8$	0.0057	0.00096
$V = 2 : V = 16$	0.0056	0.00099
$V = 4 : V = 8$	0.0054	0.00093
$V = 4 : V = 16$	0.0055	0.00100
$V = 8 : V = 16$	0.0054	0.00110
Average	0.0056	0.00099

Table LIV—K_N Found and Calculated for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N Found	K_N Calculated	Error in per cent.
1	0.00155	0.00155	0.00
2	0.00185	0.00186	—0.50
4	0.00217	0.00218	—0.50
8	0.00254	0.00253	+0.40
16	0.00290	0.00292	—0.60

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 35°

Table LV — 0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	1.09	0.00306
50	1.32	0.00305
60	1.53	0.00302
70	1.74	0.00302
80	1.98	0.00299

Average $K_V = 0.00303$
$K_N = 0.00606$

Table LVI—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.97$

t	x	K_V
40	1.09	0.00307
50	1.30	0.00300
60	1.54	0.00304
70	1.73	0.00300
80	1.92	0.00298

Average $K_V = 0.00302$
$K_N = 0.00604$

Table LVII—0.25 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 19.94$

t	x	KV
40	1.33	0.00178
50	1.60	0.00175
60	1.88	0.00174
70	2.17	0.00174
80	2.46	0.00176

Average $K_V = 0.00176$
$K_N = 0.00704$

Table LVIII—0.25 N Sodium Phenolate and 0.50 N Ethyl Iodide at 34°.9[1]

$A = 10.00$ $B = 19.96$

t	x	K_V
40	1.25	0.001728
50	1.54	0.001746
60	1.82	0.001762
70	2.08	0.001766
80	2.28	0.001725
90	2.48	0.001700

Average $K_V = 0.001738$
K_N (34°.9) $= 0.006952$
K (35°.0) $= 0.00701$

Table LIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	2.92	0.001006
60	4.14	0.000993
80	5.26	0.000988
100	6.36	0.000999
120	7.28	0.000993
140	8.20	0.000999

Average $K_V = 0.000996$
$K_N = 0.00797$

Table LX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°.1

$A = 10.00$ $B = 40.00$

t	x	K_V
50	1.82	0.001029
60	2.12	0.001021
75	2.56	0.001020
80	2.66	0.001002
90	3.00	0.001032

Average $K_V = 0.001021$
K_N(35°.1) $= 0.00817$
K_N(35°) $= 0.00807$

[1] In these experiments the temperature of the bath was 34°.9. We have therefore used the equation $K_T = K_{T_0} \times 10\,(0.0526\,T - 0.0526\,T_0)$ (Hecht and Conrad: Z. physik. Chem., **3**, 465) to correct for 35°.0.

Table LXI—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	1.78	0.000589
50	2.16	0.000579
60	2.58	0.000585
70	3.02	0.000587
80	3.31	0.000578

Average $K_V = 0.000584$
$K_N = 0.00934$

Table LXII—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°.1

$A = 20.00$ $B = 80.00$

t	x	K_V
50	2.20	0.000592
60	2.58	0.000585
70	3.04	0.000600
80	3.39	0.000593
90	3.67	0.000577

Average $K_V = 0.000590$
$K_N(35°.1) = 0.00944$
$K_N(35°) = 0.00933$

Table LXIII—K_N Found for Sodium Phenolate and Ethyl Iodide at 35°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
2	0.00604 0.00606	0.00605
4	0.00704 0.00701[1]	0.00702
8	0.00807[1] 0.00797	0.00802
16	0.00934 0.00933[1]	0.00933

Table LXIV—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.0188	0.00315
$V = 2 : V = 8$	0.0181	0.00333
$V = 2 : V = 16$	0.0185	0.00321
$V = 4 : V = 8$	0.0175	0.00359
$V = 4 : V = 16$	0.0185	0.00327
$V = 8 : V = 16$	0.0191	0.00280
Average	0.0184	0.00323

[1] These constants were calculated for 35° from the data obtained experimentally at 34°.9 and 35°.1.

Table LXV—K_N Calculated and Found for Sodium Phenolate and Ethyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.00605	0.00604	+0.2
4	0.00702	0.00698	+0.6
8	0.00802	0.00806	—0.5
16	0.00933	0.00928	+0.5

Table LXVI—Resume of All the Values for K_i and K_m

	K_i	K_m
Sodium phenolate and methyl iodide at 25°.	0.0282	0.00474
Sodium phenolate and methyl iodide at 35°	0.091	0.0131
Sodium phenolate and ethyl iodide at 25°	0.0056	0.00099
Sodium phenolate and ethyl iodide at 35°	0.0184	0.00323

CONCLUSIONS

1. In this dissertation I have shown that the theory that only the ionized portions of electrolytes are chemically active is only partially correct, and that much of the earlier work on which this theory was based was interpreted unfortunately. We should therefore consider the possibility that both the ions and the nonionized forms of electrolytes may undergo transformation with comparable velocities, which may be influenced by so-called "salt effects" and other physical factors. With this theory in mind, the work presented here was undertaken.

2. A full description of the apparatus and quantitative methods is given in the experimental portion.

3. A list of tables is given in which I present the velocities of the reactions of sodium phenolate with methyl iodide and with ethyl iodide at 25° and 35° in absolute ethyl alcohol, the concentrations varying from N/1 to N/40.

4. The proper numerical data are substituted in a general formula, $K_N = K_i\alpha + K_m(1 - \alpha)$, and the series of simultaneous equations so obtained are solved. Constant values are obtained for K_i and K_m, which represent the velocity of

transformation of unit concentrations of phenolate ions, nonionized sodium phenolate and alkyl halides. I have interpreted this fact as evidence that both the phenolate ions and the nonionized sodium phenolate react with the nonionized alkyl halides, although I wish to point out that there may be an "abnormal salt effect" not yet understood.

5. If this theory is correct, the same value should be obtained for K_i, the velocity of transformation of unit concentrations of the phenolate ions and a given alkyl halide, whether the source of the phenolate ions be the sodium, potassium, lithium or other salts. The work reported here and other studies by Mr. Shrader, which are touched on now and will be reported in detail later, are discussed on pages 14 and 15, and it is shown there that the same alkyl halide actually does give practically the same value for K_i for sodium, potassium and lithium phenolates.

6. I suspect that the values for K_i and K_m given here may involve an "abnormal salt effect," which I shall next try to determine by measuring the reaction velocities in solutions varying from N/1 to N/2048, if possible. A similar study has already been made by Dr. C. N. Myers, who has shown that *p*-bromobenzonitrile and sodium, potassium and lithium ethylates, in solutions varying from N/32 to N/2048, give the same value for K_i for the ethylate ion in these *ideal solutions*, but *apparently different uncorrected values* for K_i and K_m in the more concentrated solutions.

7. I am investigating these peculiarities, or abnormalities, of these concentrated solutions (absolute alcohol) as rapidly as possible by attempting to measure their physical properties, especially the fluidities of the solutions by Bingham's methods, the effect of added salts on the reaction velocities, and the probable extent of the solvation (alcoholation) of the reacting constituents by Washburn's methods. These *physical factors* and the *electronic phenomena* probably play a role having far greater significance than we can possibly understand with our present knowledge.

BIOGRAPHY.

Henry Clarence Robertson, Jr., was born in Charleston, South Carolina, July 15, 1888. His preparatory training was received in private and public schools of Spartanburg, South Carolina.

In 1901 he entered Wofford College, Spartanburg, and graduated in 1905 with the degree of A.B. In the year 1906 he received the degree of Master of Arts from the same institution.

In October 1907 he entered the Johns Hopkins University as a graduate student in Chemistry, his subordinate subjects being Physical Chemistry and Biology.